THE PHENOLIC INHIBITOR IN DEHYDROGENATED ROSIN ACIDS

BY

NORTON ALLEN HIGGINS

B. S., Oklahoma Agricultural and Mechanical College, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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Introduction

During the recent war Dresinate 731 was developed as an emulsifier for replacing the soap which was used in GR-S polymerization. This material, which is the sodium salt of a mixture of dehydrogenated rosin acids, has been used successfully since its inception and produces a rubber having many desirable properties; however, as first produced it suffered the disadvantage of requiring long polymerization cycles to achieve the desired conversion. An investigation into the cause of the retarded polymerization by Hays, Drake, and Pratt[1] showed that phenolic material present was responsible. The purpose of the present work was to continue the investigation in an effort to find out more about exact nature of the phenolic material. A better knowledge of its structure would allow its more effective separation from the dehydrogenated rosin acids and possibly open the way to a new group of inhibitors for use in monomer storage.

Discussion of Results

A procedure for isolation of the phenolic polymerization inhibitor in dehydrogenated rosin acids which yielded a concentrate richer in phenolic material than that reported by previous investigators has been developed, and this concentrate has been shown to retard the copolymerization of butadiene and styrene in the GR-S-10 recipe.

From a study of the ultraviolet and infrared spectra, and from the general physical and chemical properties it was shown that the phenolic material resembles menthylphenol. It was further demonstrated that menthylphenol, when added to the GR-S-10 polymerization produced a retardation of the same order as that of the phenolic material

from the resin.

In the course of this investigation several phenols were prepared and their ultraviolet spectra compared with that of the inhibitor. It was considered that the phenolic inhibitor could have arisen in three ways: first, it could have been present in the wood as such; second, it could have been formed during the processing of the rosin by the reaction of a terpene with phenol; and third, it could have been formed from a partially oxidized rosin acid when subjected to the dehydrogenation process. The first possibility was evaluated by comparing the spectrum and chemical properties of the inhibitor with those of phenols known to be present in wood and in rosin. The latter two were evaluated by preparing representative phenols and examining their spectra and properties. Thus menthyl-, bornyl-, fenchyl-, and pinylphenols were prepared as representative terpene phenols, while 2-propyl-4,5-dimethylphenol, 2-propyl-3,6-dimethylphenol, and 2,3,4,5-tetramethylphenol were prepared to serve as model compounds representing the phenols which might be formed from partially oxidized rosin acids.

Menthyl-, bornyl-, and fenchylphenols were prepared by condensation of the corresponding chloride with phenol[2]. Pinylphenol was prepared from pinene and phenol in the presence of *p*-toluenesulfonic acid. These terpene phenols were similar to the inhibitor in that they were all krypto-phenols, and their ultraviolet spectra resembled that of the inhibitor very closely.

2-Propyl-4,5-dimethylphenol was prepared by the Claisen rearrangement of allyl 4,5-dimethylphenyl ether followed by hydrogenation[3]. 2-Propyl-3,6-dimethylphenol was prepared by the same route from allyl 3,6-dimethylphenyl ether. Since in the Claisen rearrangement of allyl 4,5-dimethylphenyl ether there are two *ortho* positions to which the allyl group may migrate, it was necessary to show whether the product obtained finally was the 2-propyl isomer or the 6-propyl isomer. This was accomplished by first isomerizing the

Claisen rearrangement mixture of allylphenols to propenylphenols, followed by ozonolysis to the corresponding mixture of 4,5- and 5,6-dimethylsalicylaldehydes[4]. Since these two isomers crystallized in different forms which were easily separable, it was established that in the Claisen rearrangement the allyl group migrated 70± 5 per cent to the 2 position and 30 ± 5 per cent to the 6 position. In the preparation of 2-propyl-4,5-dimethylphenol, after the Claisen rearrangement product had been hydrogenated, 50 per cent of the mixture crystallized. Since, as was shown by the ozonolysis, the 6-propyl isomer could have accounted for only about 30 per cent of the mixture, the isomer which crystallized must have been 2-propyl-4,5-dimethylphenol.

2,3,4,5-Tetramethylphenol was prepared from isodurene as a starting material. The isodurene was sulfonated and the resulting sulfonic acid subjected to the Jacobsen rearrangement[5] to yield prehnitenesulfonic acid. This, after alkaline fusion followed by acidification, yielded 2,3,4,5-tetramethylphenol.

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VITA

The author was born in Cushing, Oklahoma, on October 24, 1920. He received his elementary education in the Stillwater, Oklahoma, public schools and in June, 1942, received the Bachelor of Science degree from Oklahoma Agricultural and Mechanical College in the same city. He was subsequently employed for three years with E. I. du Pont de Nemours and Company in Buffalo, New York. Since his entry into the Graduate College of the University of Illinois in September, 1945, he has been employed as a special research assistant on the Synthetic Rubber Research Program, Office of Rubber Reserve, Reconstruction Finance Corporation.

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